***WSC – CAM – VI A***

# Quality Assurance and Quality Control Requirements and Performance Standards for ***SW-846 Method 9014***, **Total Cyanide and the MADEP Physiologically Available Cyanide (PAC) Protocol**, for the Massachusetts Contingency Plan (MCP)

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Donald Muldoon
Department of Environmental Protection
One Winter Street
Boston, MA 02108
donald.muldoon@state.ma.us


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VI. Miscellaneous Wet Chemical Methods

## A. Quality Assurance/Quality Control (QA/QC) Requirements and Performance Standards for SW-846 Method 9014 for Total Cyanide and the MADEP Physiologically Available Cyanide (PAC) Protocol

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## 1.0 QA/QC Requirements for SW-846 Method 9014 and the MADEP PAC Protocol

1.1 Overview of Methods

Free (non-complexed) cyanide and hydrocyanic acid in solution may be readily determined spectrophotometrically or by titration in water, soil and wastes using EPA SW-846 Method 9014. This Method may be used as the determinative step for quantifying Total Cyanide, and with minor modifications for Physiologically Available Cyanide (PAC), in alkaline distillates from Methods SW-846 9010 and the MADEP PAC Protocol. These distillation procedures are described in detail in Section 1.2. The Total Cyanide method is applicable for the determination of simple and complex cyanides, including iron-cyanide complexes, released during the rigorous distillation/digestion procedure. The PAC method is applicable to the determination of biologically (physiologically) available cyanides (excluding iron-cyanides), released during the PAC digestion procedure. All references to SW-846 methods in this document refer to the United States Environmental Protection Agency's most recently published version.

Analytical Note: Method 4500-$CN^-$, Standard Methods for the Examination of Water and Wastewater (Part 4000, 20th Edition), is considered equivalent to SW-846 Method 9014 as a determinative step for Total Cyanide. Method 4500-$CN^-$ should be consulted for a more detailed discussion of method interferences.

1.1.1 Reporting Limits for SW-846 Method 9014 and MADEP PAC Protocol

Reporting Limits (RL), sensitivity, and/or the optimum linear concentration range can vary with the cyanide compound or complex, sample matrix and laboratory operating conditions.

The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide or PAC exceeding 0.1 mg/L (equivalent to a concentration of 0.025 mg/250 mL in absorbing liquid). It should be noted that this sensitivity does not meet MCP GW-3 Method 1 Cleanup Standard of 0.01 mg/L; as described in Section 4.0, Regulatory Limits for Cyanide under 310 CMR 40.000. The spectrophotometric method should be used in all cases to evaluate regulatory compliance with the MCP.

The colorimetric (spectrophotometric) procedure is used for concentrations below 1 mg/L of cyanide or PAC and is suitable to determine compliance with the GW-3 Method 1 Standard of 0.01 mg/l, see Section 4.0.

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for trace metals analyzed in support of MCP decision-making are presented in Appendix VI A–1 of this document and Appendix VII-A, WSC-CAM-VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)".

1.1.2 General Quality Control Requirements of SW-846 Method 9014 and The MADEP PAC Protocol

Each laboratory that uses SW-846 Method 9014 and the MADEP PAC Protocol are required to operate a formal quality assurance program to demonstrate the precision and bias of the method as performed by the laboratory and procedures for determining the method reporting limit (RL). The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of laboratory control samples (LCSs), and LCS duplicates to assess accuracy and/or precision. Project-specific matrix duplicates or matrix spike duplicates (MSDs) may be used in lieu of LCS duplicates to evaluate precision when such samples are analyzed either at discretion of laboratory or at request of data-user. Refer to SW-846 Methods 9010B, 9013 and 9014 Sections 8.0 and 9.0 for general quality control guidelines for these cyanide determinative methods.

Laboratories must document and have on file an Initial Demonstration of Capability for each combination of sample preparation and determinative cyanide method being used. These data must meet or exceed the performance standards as presented in Section 1.4 and Table VI A-1 of this method. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in SW-846, Chapter One, Section 4.4.1. The data associated with the Initial Demonstration of Capability for Total Cyanide and PAC analyses must be kept on file at the laboratory and made available to potential data-users on request and must include the following:

| QC Element | Performance Criteria |
|---|---|
| Initial Calibration | WSC-CAM–VI A, Table VI A-1 |
| Continuing Calibration | WSC-CAM–VI A, Table VI A-1 |
| Method Blanks | WSC-CAM–VI A, Table VI A-1 |
| % Percent Recovery for MS/LCS | WSC-CAM–VI A, Table VI A-1 |
| Relative Percent Difference (RPD) for MSD/LCS Duplicate | WSC-CAM–VI A, Table VI A-1 |
| Internal Standards | WSC-CAM–VI A, Table VI A-1 |
| Positive/Negative Laboratory Controls (PAC only) | WSC-CAM–VI A, Table VI A-1 |

Laboratories are encouraged to continually strive to minimize variability and improve the accuracy and precision of their analytical results. In some cases, the standard laboratory acceptance criteria for the various QC elements may have to be modified to accommodate more rigorous project-specific data quality objectives prescribed by the data user. The laboratory may be required to modify routine sample introduction and/or analytical conditions to accommodate project-specific data quality objectives.

Use of this method is restricted to use by, or under the supervision of, analysts who are knowledgeable of spectrophotometry and titration procedures as quantitative tools and the correction of the chemical, and physical interferences described in this method.

1.2 Summary of Methods

1.2.1 Cyanide Digestion Methods

The aggressiveness of the sample digestion associated with the method selected determines the range of cyanide salts and insoluble cyanide complexes that will ultimately be decomposed captured in the absorber solution and detected by the selected determinative method. Total Cyanide by SW-846 Method 9010B; using catalytic, concentrated mineral acid reflux distillation is the most aggressive (measuring almost all cyanide forms) while the Massachusetts PAC Protocol; simulating the human digestive system; is the least aggressive (measuring only simple cyanides and excluding iron-cyanide complexes).

1.2.1.1 SW-846 Method 9010B Reflux-Distillation Procedure

Analytical Note: The RCRA-defined "reactive" cyanide content of a waste, that is, the cyanide content that could generate toxic fumes when exposed to mild acidic conditions, is not determined by this method. Refer to Chapter Seven of SW-846 for the additional information on reactive cyanide.

SW-846 Method 9010B is a reflux-distillation procedure used to extract soluble cyanide salts and many insoluble cyanide complexes (i.e., iron-cyanides) from waters, soils, wastes and leachates. It is based on the decomposition of nearly all cyanides by a reflux distillation procedure using a concentrated mineral acid and a magnesium catalyst. Cyanide, in the form of hydrocyanic acid (HCN) is purged from the sample and captured into an alkaline scrubber solution. The concentration of cyanide in the scrubber solution is then determined by EPA SW-846 Method 9014 or an equivalent micro-distillation procedure modification of this method, using reduced sample and reagent volumes to minimize hazardous waste generation, either spectrophotometrically or titrametrically depending on the concentration of the sample. The reflux-distillation procedure described in SW-846 Method 9010B may be used for both total cyanide and cyanide amenable to chlorination analyses (see reference methods for details).

1.2.1.2 MADEP Physiologically Available Cyanide (PAC) Protocol

The MADEP PAC Protocol is a performance based reflux-distillation procedure that is used for the determination biologically available cyanides and is intended to simulate the inter-action of the human digestive system and ingested cyanide complexes. PAC is defined as the quantity of cyanide released during digestion/distillation under the conditions specified by the test protocol (see Appendix VI A-2). The cyanide forms released in this digestion include free cyanide, simple cyanide complexes (such as cyanide salts) and certain metal

cyanides, with the exception of iron-cyanide complexes (including "Prussian Blue"), that are not readily released under the analytical conditions of this procedure.

The cyanide released during the PAC digestion in the form of hydrocyanic acid (HCN) is purged from environmental samples under mildly acidic ($1.25 \leq pH \leq 2.0$), buffered and catalyzed digestion conditions and captured into an alkaline scrubber solution. The concentration of cyanide in the scrubber solution is then determined by a "modified" (inclusion of positive and negative laboratory control samples) SW-846 Method 9014 either spectrophotometrically or titrametrically depending on the concentration of the sample.

Method performance is controlled by the temperature ($78 \pm 3^{o}$ C) and flow rate ($300 \pm 30$ cc/min) guidelines described in the Protocol. The flow rate would be proportionately lower for midi-distillation procedure. Method performance is verified by the evaluation of the Percent Recovery (%R) of Positive and Negative Laboratory Control Samples analyzed under the controlled test parameters and digestion specifications of the Protocol. Potassium Cyanide (KCN) is used as the Positive Laboratory Control Sample (LCS-P) and Prussian Blue is used as the Negative Laboratory Control Sample (LCS-N) for the PAC Protocol. Acceptable percent recovery (% R) criteria for LCS-P and LCS-N are $100 \pm 20$ and $\leq 10$, respectively. Refer to Appendix VI A-1, DRAFT MADEP Physiologically Available Cyanide (PAC) January 1996 Protocol for specific analytical details. The Positive Laboratory Control Sample (LCS-P) of the PAC Protocol is equivalent to the Laboratory Control Sample (LCS) for EPA SW-846 Method 9014.

1.2.2 Cyanide Determinative Methods

The titration measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator, p-dimethylamino-benzal-rhodanine. When all of the cyanide has complexed and more silver nitrate is added, the excess silver combines with the rhodanine indicator to turn the solution yellow and then brownish-pink.

Analytical Note: This titration is based on the following reaction:

$$Ag^{+} + 2CN^{-} \longrightarrow [Ag(CN)_2]^{-}$$

In the spectrophotometric procedure, the cyanide is converted to cyanogen chloride (CNCl) by reaction of cyanide with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 578 nm for the complex formed with pyridine-barbituric acid reagent and CNCl. To obtain colors of comparable intensity, it is essential to have the same reagent concentrations in both the sample and the standards.

| | |
|---|---|
| Analytical Note: | SW-846 Method 9012A, Total and Amenable Cyanide (Automated Colorimetric, with Off-Line Distillation), is considered equivalent to SW-846 Method 9014 as a determinative step for both Total Cyanide and PAC. The quality control requirements and performance standards described in Table VI A –1 may be applied directly to this method. |

1.3 EPA SW-846 Method 9014 and MADEP PAC Protocol Interferences

Potential analytical interferences and their recommended corrective measures for both extraction and analytical procedures for cyanide are summarized below and presented in detail in Section 3.0 of SW-846 Method 9010B. Many of these potential Interferences for Total Cyanide or PAC may be eliminated or substantially reduced during the reflux distillation procedure described in Section 7.2 of SW-846 Method 9010B.

1.3.1 Oxidizing agents such as chlorine decompose most cyanide compounds and complexes. Chlorine interferences can be removed by adding an excess of ascorbic acid or sodium arsenite to aqueous samples prior to preservation and storage to reduce the chlorine ($Cl_2$) to non-interfering chloride ($Cl^-$).

1.3.2 Sulfide interference can be removed by adding an excess of bismuth nitrate to the samples (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

Analytical Note: See SW-846 Method 9014, Section 7.4 for preparation of standard curves for sulfide containing samples. Special analytical steps include:

- Standards must be distilled
- Use Method of Standard Additions
- Minimum of five (5) dynamic standards

1.3.3 Positive interferences for cyanide (high bias results) may be obtained for samples that contain nitrate and/or nitrite at concentrations exceeding 10 mg/L. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds will decompose under test conditions to generate hydrocyanic acid (HCN). The possibility of interference by nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Special caution should be exercised if bismuth nitrate is used to remove sulfide interference (see Section 1.3.2)

1.3.4 Thiocyanate is reported to be interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

1.3.5 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in high concentrations and may make the endpoint for

the titrimetric determination difficult to detect. Refer to Sec. 6.8 of Method SW-846 9010B for an extraction procedure to eliminate this interference.

1.3.6 Samples containing solids of an amount and/or size as to interfere with agitation and homogenization of the sample mixture in the distillation flask, or so much oil or grease as to interfere with the formation of a homogeneous emulsion may be extracted with water (and hexane if heavy grease is present) at pH 10 or greater to minimize this potential interference as described in SW-846 Method 9013, Cyanide Extraction Procedure for Solids and Oils**.** This extract should be analyzed by SW-846 Method 9010B.

1.3.7 Some cyanide complexes, such as Potassium Ferricyanide, $K_3$ [Fe-$(CN)_6$, may be susceptible to photodecomposition when exposed to fluorescent lighting or sunlight during sample handling and/or analysis. This photodecomposition can change the type of the cyanide compounds in the sample, which is critical for the PAC method (such a change will not affect Total CN measurements). Therefore, if PAC is being measured, due caution must be exercised to limit the exposure of the sample to light to maintain the integrity of sample from collection through analysis.

1.4 Specific QA/QC Requirements and Performance Standards for SW-846 Method 9014 and The MADEP PAC Protocol

Specific QA/QC requirements and performance standards for SW-846 Method 9014 and The MADEP PAC Protocol are presented in Table VI A-1. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide a data user with “Presumptive Certainty” regarding the usability of analytical data to support MCP decisions. The concept of “Presumptive Certainty” is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of “Presumptive Certainty” of data acceptance by agency reviewers. In order to achieve “Presumptive Certainty”, parties must:

(a) Comply with the procedures described and referenced in WSC-CAM–VI A;

(b) Comply with the applicable QC analytical requirements prescribed in Table VI A-1 for this test procedure;

(c) Evaluate, and narrate, as necessary, compliance with performance standards prescribed in Table VI A-1 for this test method; and

(d) Adopt the reporting formats and elements specified in the CAM

In achieving the status of “Presumptive Certainty”, parties will be assured that analytical data sets:

- ✓ Will satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data;

- ✓ May be used in a data usability assessment, and if in compliance with all MCP Analytical Method standards, laboratory QC requirements, and field QC recommended limits and action levels, the data set will be considered useable data to support site characterization decisions made pursuant to the MCP; and

- ✓ May be used to help support a data representativeness assessment.

Widespread adherence to the "Presumptive Certainty" approach will promote inter-laboratory consistency and provide the regulated community with a greater degree of certainty regarding the quality of data used for MCP decision-making. The issuance of these requirements and standards is in no way intended to preempt the exercise of professional judgement by the LSP in the selection of alternative analytical methods. However, parties who elect not to utilize the "Presumptive Certainty" option have an obligation, pursuant to 310 CMR 40.0017 and 40.0191(2)(c), to demonstrate and document an overall level of (laboratory and field) QA/QC, data usability, and data representativeness that is adequate for and consistent with the intended use of the data.

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| Required QA/QC | Data Quality Objective | Performance Standard | Required Deliverable | Recommended Corrective Action | Analytical Response Action |
|---|---|---|---|---|---|
| Preparation of Samples | Accuracy and Representativeness | For Total and Physiologically Available Cyanide (PAC), all aqueous and solid samples must be pretreated prior to analysis. See EPA Methods SW-846 9010B and MADEP PAC Protocol for appropriate reflux distillation procedures. | No | | |
| Initial Calibration | Laboratory Analytical Accuracy | (1) Frequency – Daily or each time instrument is set up, prior to sample analysis using KCN standards Minimum of a calibration blank plus five un-distilled calibration standards.<br>(2) Low-level standard in calibration must be at the laboratory reporting limit (RL)<br>(3) Linear curve fit with correlation coefficient $r \geq 0.995$. Must have the same reagent content in both the sample and the standards (matrix-matched).<br>(4) If titration procedure is used, the silver nitrate solution must be standardized as described in "Standard Methods for the Examination of Water and Wastewater," Method 4500-CN D. | No | Recalibrate as required by method. | |
| Initial Calibration Verification (ICV) | Laboratory Analytical Accuracy | (1) Frequency – **Daily following the initial calibration and prior to sample analysis.**<br>(2) Separate-source from calibration standards and distilled with samples in batch.<br>(3) Mid-calibration range standard, or vendor supplied value.<br>(4) ICV percent recovery must be 85-115% | No | Recalibrate/reanalyze ICV as required by method. | Suspend all analyses until Initial Calibration non-conformance is rectified. |

| Required QA/QC | Data Quality Objective | Performance Standard | Required Deliverable | Recommended Corrective Action | Analytical Response Action |
|---|---|---|---|---|---|
| Continuing Calibration Verification (CCV) | Laboratory Analytical Accuracy | (1) Frequency - Every 10 field samples and at end of analytical run.<br>(2) Same-source as calibration standards; Un-distilled standard near mid-point of calibration range<br>(3) CCV percent recovery must be 85-115% | No | Recalibrate/reanalyze all samples since last compliant CCV. | Narrate noncompliance. |
| Continuing Calibration Blank (CCB) | Laboratory Analytical Sensitivity (instrument drift and contamination evaluation) | (1) Frequency - Every 10 field samples following CCV and at end of analytical run. Run immediately after CCV<br>(2) Must be matrix-matched (the same concentration of reagents as standards and samples); not distilled<br>(3) CCB must be < RL | No | Recalibrate/reanalyze all samples since last compliant CCB. | Narrate noncompliance. |
| Method (Preparation) Blank | Laboratory Method Sensitivity (contamination evaluation) | (1) Frequency - One per digestion batch of ≤ 20 field samples.<br>(2) Must be matrix-matched (the same concentration of reagents as calibration and QC standards) and distilled with samples in batch<br>(3) Method Blank must be < RL | Yes | Redigest/reanalyze all associated samples unless all detected results are > 10x method blank level. | Narrate noncompliance. |
| Laboratory Control Sample (LCS) for Total Cyanide, and Positive Laboratory Control Sample (LCS-P) for PAC | Laboratory Method Accuracy, and Method Performance for PAC | (1) Frequency – One per digestion batch of ≤ 20 field samples.<br>(2) Medium calibration range (75%) standard, or vendor supplied value for Total Cyanide and 0.1 mg/L for PAC.<br>(3) LCS must be matrix-matched (soil or water) to field samples and digested with samples.<br>(4) LCS and LCS-P must be distilled with samples in batch. Positive LCS = KCN.<br>(5) LCS and LCS-P percent recovery must be 80-120%. | Yes | Redigest/reanalyze all associated samples. | If LCS-P (for PAC) or LCS (for Total Cyanide) are not within criteria, then method protocol is unacceptable; re-distill and re-analyze all associated batch samples to obtain acceptable positive and negative LCSs for PAC or LCS for Total Cyanide. |

| Required QA/QC | Data Quality Objective | Performance Standard | Required Deliverable | Recommended Corrective Action | Analytical Response Action |
|---|---|---|---|---|---|
| LCS Duplicate for Total Cyanide, and LCS-P Duplicate for PAC | Laboratory Method Precision | (1) Frequency – One per digestion batch of ≤ 20 field samples.<br>(2) Prepared using same standard source and concentration as LCS..<br>(3) LCS must be distilled with samples in batch. Positive LCS = KCN.<br>(4) Recommended to be run immediately after LCS in analytical sequence.<br>(5) LCS duplicate must be matrix-matched to samples (aqueous/solid) and digested with the samples<br>(6) Laboratory–determined Relative Percent Difference (RPD) must be ≤ 20 (aqueous) and ≤ 35 (soils/sediments), and<br>(7) A project-specific MD or MSD may be substituted to evaluate precision in lieu of an LCS duplicate. | Yes | Re-digest/reanalyze all associated samples. | If LCS-P (for PAC) or LCS (for Total Cyanide) are not within criteria, then method protocol is unacceptable; re-distill and re-analyze all associated batch samples to obtain acceptable positive and negative LCSs for PAC or LCS for Total Cyanide. |
| Negative Laboratory Control Sample For PAC<br>(LCS-N) | Method Performance for PAC only | (1) Frequency - One per digestion batch of ≤ 20 field samples.<br>(2) **LCS-N must be distilled with samples in batch. Negative LCS-N = Prussian Blue (Iron-cyanide)**<br>(3) **Concentration LCS-N = 1.0 mg/L**<br>(4) LCS-N percent recovery for must be ≤ 10 % | Yes | Re-digest/reanalyze all associated samples. | If LCS-N is not within criteria, then PAC method protocol is unacceptable; re-distill and re-analyze all associated batch samples to obtain acceptable positive and negative LCSs. |
| Project Specific Matrix Spike Sample<br>(MS) | Method Accuracy in Sample Matrix | (1) Frequency - One per digestion batch of ≤ 20 field samples at the discretion of the laboratory or at the request of data user.<br>(2) Percent Recoveries must be between 75 – 125 % for all media<br>(3) Laboratories are expected to develop their own in-house control limits for each media, which should fall within the limits listed above. | Yes, if MS requested by data user or run by laboratory as routine QA/QC | No corrective action required. | Narrate noncompliance |

| Required QA/QC | Data Quality Objective | Performance Standard | Required Deliverable | Recommended Corrective Action | Analytical Response Action |
|---|---|---|---|---|---|
| Project Specific Matrix Spike Duplicate Sample*<br><br>(MSD) | Method Precision in Sample Matrix | (1) Frequency - One per digestion batch of ≤ 20 field samples at the discretion of the laboratory or at the request of data user.<br>An MD sample may be substituted* for an MSD under some circumstances.<br>(2) MSD relative percent difference (RPD) criteria: aqueous results: ≤ 20%; soil and sediment results: ≤ 35%. | Yes, if MSD requested by data user or run by laboratory as routine QA/QC | No corrective action required. | Narrate noncompliance |
| Project Specific Matrix Duplicate Sample*<br><br>(MD) | Method Precision in Sample Matrix | (1) Optional (may be done in lieu of MSD)- One per digestion batch of ≤ 20 field samples.<br>(2) MD relative percent difference (RPD) criteria recommended: aqueous results > 5x RL: ≤ 20%; aqueous results < 5x RL: difference ≤ RL; soil and sediment results > 5x RL: ≤ 35%; soil and sediment results < 5x RL: difference ≤ 2x RL. | Yes, if MD requested by data user or run by laboratory as routine QA/QC | No corrective action required. | Narrate noncompliance. |
| * A matrix duplicate analysis should be performed if cyanide is suspected to be present in a sample. It is recommended that a matrix spike duplicate analysis be performed in lieu of a matrix duplicate, if cyanide is **not** suspected to be present in a sample. | | | | | |
| Sample Quantitation and General Reporting | NA | (1) Non-detected values must be reported with the sample-specific reporting limit for each analyte.<br>(2) The RL must be supported by the low-level standard in the calibration curve.<br>(3) Results for solid matrices must be reported on a dry-weight basis to compare to MCP standards.<br>(4) Sample concentrations that exceed the calibration range must be diluted to fall within the calibration range when re-analyzed, or, may be re-distilled at a lesser initial volume/weight. | Yes | Not applicable. | Not applicable |

## 2.0 Data Usability Assessment for SW-846 Method 9014 and the MADEP PAC Protocol

Overall data usability is influenced by uncertainties associated with both sampling and analytical activities. This document provides detailed quality control requirements and performance standards for SW-846 Method 9014 and the MADEP PAC Protocol which may be used to directly assess the analytical component of data usability. The sampling component of data usability, an independent assessment of the effectiveness of sampling activities to meet data quality objectives, is not substantively addressed in this document.

## 3.0 Reporting Requirements for SW-846 Method 9014 and the MADEP PAC Protocol

3.1 General Reporting Requirements for SW-846 Method 8260B

General reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM-VIIA. This guidance document provides recommendations for field QC, as well as the required content of the Environmental Laboratory Report, including

- Laboratory identification information presented in WSC-CAM-VII A, Section 2.4.1,
- Analytical results and supporting information in WSC-CAM-VII A, Section 2.4.2,
- Sample- and batch-specific QC information in WSC-CAM-VII A, Section 2.4.3,
- Laboratory Report Certification Statement in WSC-CAM-VII A, Section 2.4.4,
- Copy of the Analytical Report Certification Form in WSC-CAM-VII A, Exhibit VII A-1,
- Environmental Laboratory case narrative contents in WSC-CAM-VII A, Section 2.4.5,
- Chain of Custody Form requirements in WSC-CAM-VII A, Section 2.4.6

3.2 Specific Reporting Requirements for SW-846 Method 9014 and the MADEP PAC Protocol

Specific Quality Control Requirements and Performance Standards for SW-846 Method 9014 and the MADEP PAC Protocol are presented in Table VI A-1. Specific reporting requirements for SW-846 Method 9014 and the MADEP PAC Protocol are summarized below in Table VI A-2 as "Required Analytical Deliverables (**YES**)". These routine reporting requirements should always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as "Required Analytical Deliverables (**NO**)", these data are to be available for review during an audit and may also be requested on a client-specific basis

**Table VI A-2 Routine Analytical Reporting Requirements for SW-846 Method 9014B and the MADEP Physiologically Available Cyanide (PAC) Protocol**

| Parameter | Required Analytical Deliverable |
|---|---|
| | |
| Preparation of Samples | ***NO*** |
| Initial Calibration | ***NO*** |
| Initial Calibration Verification (ICV) | ***NO*** |
| Initial Calibration Blank (ICB) | ***NO*** |
| Continuing Calibration Verification (CCV) | ***NO*** |
| Continuing Calibration Blank (CCB) | ***NO*** |
| Method (Preparation) Blank | ***YES*** |
| Total Cyanide Laboratory Control Sample (LCS) | ***YES*** |
| Positive Laboratory Control Sample (LCS-P) | ***YES (PAC only)*** |
| Total Cyanide LCS Duplicate | ***YES*** |
| LCS-P Duplicate | ***YES (PAC only)*** |
| Negative Laboratory Control Sample (LCS-N) | ***YES (PAC Only)*** |
| Project Specific Matrix Spike Sample (MS) | ***YES (if requested by data user)*** |
| Project Specific Matrix Spike Duplicate (MSD) | ***YES (if requested by data user)*** |
| Project Specific Field Matrix Duplicate (MD) | ***YES (if requested by data user)*** |
| General Reporting | ***YES*** [1] |

***1. Non-detected concentrations, must be reported as less than the sample-specific reporting limit (< RL) that is, supported by low-level calibration standard.***

## 4.0 Regulatory Limits for Cyanide Under 310 CMR 40.000

The most stringent (lowest) MCP Reportable Concentrations (RCs) and Method 1 Groundwater and Soil Standards for Cyanides analyzable by SW- 846 Method 9014 and the Massachusetts Physiologically Available Cyanide Protocol (See Appendix VI A-2) are as follows:

Regulatory Limits for Cyanide under 310 CMR 40.0000

| Metal | RQ Pounds | RC GW-1 mg/L - (ppm) | RC S-1 mg/kg - (ppm) | Method 1 Groundwater ug/L - ppb | Method 1 Soils ug/g - ppm |
|---|---|---|---|---|---|
| Cyanide | 5[a] | 0.01 [a] | 100 [a] | 10[b] (GW-3)<br>200 [b] (GW-1) | 100 [b] (S-1 and S-2 Standards) |

a. (CASN: 00057-12-5, expressed as Cyanides; Isocyanide; Cyanide ion; Cyanide anion; Cyanides, inorganic, n.o.s.; Cyanide ($CN^-$). Total Cyanide[1], SW-846 Method 9014, is recommended to evaluate compliance with the notification requirements of 310 CMR 40.0330.

b. Expressed as Free[2] or Physiologically Available Cyanide (PAC)[3]. Total Cyanide may be used as a conservative estimate of Free Cyanide or PAC.

NOTE: In the proposed changes to the MCP Numerical Standards, dated 20 December 2001, the following change has been proposed to the footnotes of MCP Table I, 310 CMR 40.0974(2); Table 2, 310 CMR 40.0975(6)(a); Table 3, 310 CMR 40.0975(6)(b); Table 4, 310 CMR 40.0975(6)(c); Table 5, 310 CMR 40.0985(6); and Table 6, 310 CMR 40.0996 (7) :

> Cyanide expressed as Physiologically Available Cyanide (PAC). In the absence of measured Physiologically Available Cyanide, the standard is applicable to Total Cyanide.

RQ – Reportable Quantity
RC – Reportable Concentration for Groundwater (GW-1) and Soils (S-1)
Method 1 Groundwater – GW-1 Category unless otherwise noted
Method 1 Soils – Category S-1/GW-1 in all cases
NS – No MCP Method 1 Standard has been promulgated by the Department.

1. Total Cyanide includes Free Cyanide plus nitriles (organic cyanides) and other simple cyanides, such as cyanide salts, and stable metallo-cyanide complexes including iron-cyanides. Total Cyanide is defined as the sum of cyanides, as hydrocyanic acid (HCN), released during the aggressive catalytic, mineral acid reflux distillation procedure described in SW-846 Method 9014.

2. Free Cyanide (non-complexed) is defined as the sum of cyanide, as hydrocyanic acid (HCN), and cyanide ion ($CN^-$), expressed as $CN^-$. Free Cyanide may be determined using SW-846 Method 9213. ***This method does not include reflux distillation***.

3. Physiologically Available Cyanide as determined by the Massachusetts PAC protocol, includes biologically available cyanides that are released during this protocol distillation including free cyanide, simple cyanide salts, and some metal-cyanides that are easily dissociated. This protocol will not release iron-cyanide complexes from samples.

Appendix VI A - 1

## Sample Collection, Preservation, And Handling Procedures for Total and Physiologically Available Cyanide (PAC) Analysis

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil and sediment Total Cyanide and PAC samples analyzed in support of MCP decision-making are summarized below in Table VI A – 3 and presented in Appendix VII -A, CAM-VII A, "Quality Assurance and Quality Control Guidelines for Sampling, Data Evaluation and Reporting Activities for the Massachusetts Contingency Plan (MCP)..

**Table VI A - 3 Holding Times and Preservatives for Cyanide Samples**

| {PRIVATE} Matrix | Container | Preservation | Holding Time |
|---|---|---|---|
| Aqueous Samples | 250 mL Polyethylene for mini-distillation procedure;<br>1 L Poly for maxi-distillation | NaOH to pH ≥ 12.0.<br>Cool to 4 ± 2°, 0.6 g ascorbic acid per liter, if residual chlorine is suspected | 14 days |
| Soil/Sediments Samples | 4-ounce glass jar with inert (Teflon) liner | Cool to 4 ± 2° C | 14 days |
| Waste Samples [a,b] | 250 mL amber wide-mouth jar with inert (Teflon) liner | Cool to 4 ± 2° C.<br>Keep out of direct light | Soon as Possible |

a. Reactive Cyanide waste defined as 250 mg/kg of Releasable Cyanide as measured by SW-846, Chapter Seven, Section 7.3.3

b. Samples containing, or suspected of containing, cyanide or a combination of cyanide and sulfide wastes should be collected with a minimum of aeration. The sample container should be filled completely, excluding all headspace, and capped. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

# DRAFT
# METHOD FOR THE DETERMINATION{PRIVATE }

# OF Physiologically Available Cyanide (PAC)

**Massachusetts Department of Environmental Protection**

**Division of Environmental Analysis**
**(Senator William X. Wall Experiment Station)**

**Office of Research and Standards**

**Bureau of Waste Site Cleanup**

**Commonwealth of Massachusetts**

**Executive Office of Environmental Affairs**
**Ellen Roy Herzfelder**
**Secretary**

**Department of Environmental Protection**
**Robert W. Golledge**
**Commissioner**

**July 1996**
**With minor typographical edits July 2004**

# DRAFT METHOD FOR THE DETERMINATION OF Physiologically Available Cyanide (PAC)

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**{**PRIVATE **}DISCLAIMER**

Mention of trade names or commercial products does not constitute endorsement by the Massachusetts Department of Environmental Protection (MADEP). Trade names and commercial products specified within this method are based upon their use in validation studies conducted by MADEP. Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exist or have been produced documenting equivalent or superior performance.

**Method Overview**

The MADEP Physiologically Active Cyanide (PAC) Protocol is a performance based reflux-distillation procedure that is used for the determination biologically available cyanides and is intended to simulate the inter-action of the human digestive system and ingested cyanide complexes. PAC is defined as the quantity of cyanide released during digestion/distillation under the conditions specified by the test protocol. The cyanide forms released in this digestion include free cyanide, simple cyanide complexes (such as cyanide salts) and certain metal cyanides; with the exception of iron-cyanide complexes (including "Prussian Blue") that are not released under the analytical conditions of this procedure.

The cyanide released during the PAC digestion in the form of hydrocyanic acid (HCN) is purged from environmental samples under mildly acidic ($1.25 \leq pH \leq 2.0$), buffered and catalyzed digestion conditions and captured into an alkaline scrubber solution. The concentration of cyanide in the scrubber solution is then determined by a "modified" (inclusion of positive and negative laboratory control samples) SW-846 Method 9014B analysis either spectrophotometrically or titrametrically, depending on the concentration of the sample.

Method performance is assured by strict adherence to the temperature ($78 \pm 3^{o}$ C) and flow rate [300 ± 30 cc/min (proportionately lower for midi-distillation)] control guidelines specified in the Protocol and verified by the evaluation of the Percent Recovery (%R) of Positive and Negative Laboratory Control Samples analyzed under the controlled test parameters and digestion specifications of the Protocol. Potassium Cyanide (KCN) is used as the Positive Laboratory Control Sample (LCS-P) and Prussian Blue is used as the Negative Laboratory Control Sample (LCS-N) for the PAC Protocol. Acceptable percent recovery (% R) criteria for LCS-P and LCS-N are 100 ± 20 and 10, respectively. The Positive Laboratory Control Sample (LCS-P) of the PAC Protocol is equivalent to the Laboratory Control Sample (LCS) for EPA SW-846 Method 9014.

In this document detailed instructions for the manual PAC cyanide digestion/distillation procedure are presented. For alternative micro semi-automatic PAC cyanide distillation procedures follow manufacturer's instructions regarding adjusting the volume of analytical reagents.

**1.0 Sample Preparation**

1.1 Soil and Sediment Analysis

Soil and sediment samples should be analyzed as received and results reported on a dry-weight basis. Soil and sediment samples should first be passed through #10 sieve. Any material retained on the sieve should be discarded. The sieved sample should then be homogenized by stirring with stainless steel spoon or placing in mechanical

stirring device. Sample size for soil or sediment should be at least 10 grams (w/w) (1 gram for microanalyses). In no case should the PAC concentration exceed 20 mg/L in reaction flask. A % solids analysis should be conducted on a separate soil or sediment sample aliquot to allow for reporting PAC results on a dry-weight basis.

If required, solid and oily waste samples may be extracted prior to analysis by SW-846 Method 9013. This method uses a dilute sodium hydroxide solution (pH ≥ 12) as the extractant and results are reported as "extractable" cyanide.

1.2 Aqueous Analysis

Under most circumstances, aqueous samples for PAC analysis require no special preparation. Place 500 mL (50 mL for microanalyses) of the aqueous sample directly into the 1-liter Reaction Flask. The PAC concentration in the reaction flask must never exceed 20 mg/L. A sample aliquot may be diluted appropriately with distilled water to a final volume of 500 mL to accommodate this requirement.

**2.0 Reagent Preparation**

*Phosphate Buffer Solution*. Dissolve 500 grams of $NaH_2PO_4.H_20$ to 500 mL of distilled water in a one-liter beaker. With the electrode of a pH meter immersed in the solution, concentrated phosphoric acid is added until the pH reaches and stabilizes under stirring at 1.25.

*Magnesium Chloride ($MgCl_2$) Solution (2.5M).* Dissolve 510 g of $MgCl_2.6$ H2O in 1-liter of distilled water..

*Sodium Hydroxide Solution (1.25N).* Dissolve 50 g of NaOH in 1-liter of distilled water.

**3.0 Apparatus and Materials**

The required apparatus and material for PAC analysis are described in Section 4.0, SW-846 Method 9010B, Total and Amenable Cyanide: Distillation. As in other published Total and Weak & Dissociable Cyanide determinative methods, Cyanide, as hydrocyanic acid (HCN), is released from samples by acid hydrolysis and captured in an alkaline mediated gas scrubber under vacuum. Additional requirements of the PAC method are as follows:

- ✓ Samples should be analyzed in a fume hood,
- ✓ A flow meter should be placed at the air inlet, and
- ✓ Equipment should be set-up in thermostatically controlled constant temperature bath.

Some analysts may control temperature by other means, such as thermostatically controlled constant temperature heating blocks, or heating mantles with thermostatically controlled voltage regulators. Manual temperature control is less preferable, but allowable if fully documented.

**4.0 Sample Digestion and Distillation**

4.1 An aliquot of 10.0 ± 0.1 g (w/w) of soil/sediment or 500 mL of aqueous sample (or sample diluted to 500 mL) is placed directly in the 1-liter reaction flask. For soil and sediment samples, the weighing container is thoroughly rinsed with distilled water to ensure complete sample transfer and brought to a final analytical volume of 500 mL. Add the distilled water with manual swirling to ensure complete surface contact.

4.2 Add 50 mL of the sodium hydroxide solution (1.25N) and 10-15 mg of $CdCO_3$ to a gas scrubber equipped with a coarse frit. Connect the reaction flask, condenser, gas scrubber and vacuum trap. Set temperature of thermostatically controlled constant temperature bath to 78 ± 3° C. When bath has equilibrated at 78 degrees, place the reaction flask in the bath and apply vacuum to initiate gas flow through gas scrubber.

4.3 Add 75 mL of the phosphate buffer, 2 g of sulfamic acid, and 20 mL of $MgCl_2$ solution through the inlet tube. Test the pH of the solution in the reaction flask to verify that the pH is ≥ 2.0. Place the thermometer in the inlet tube to record the temperature of the solution in the reaction flask. .

4.4 Record the reaction flask temperature every 15 minutes. Maintain the temperature at 78 ± 3° C for a period of **one hour**. Record total reaction time (the total time that the flask is in the water bath). Airflow should be measured at least every 15 minutes. Flow should be adjusted so that a 300 ± 30 mL/min flow is maintained on average for the total reaction time. Care should be taken that the sodium hydroxide solution in the gas scrubber does not bubble over.

4.5 After the one hour of reaction time, turn off heating source and allow sample to come to room temperature. Measure the pH of the solution in the reaction flask electrochemically to verify that the pH was maintained between 1.25 and 2.0 during the total reaction time. Test the absorber solution with lead acetate paper for excess sulfide before analysis. Treat with bismuth nitrate, as necessary. .

Analytical Note: The analyst must be continually aware of the potential for cross-contamination. Measured PAC concentrations are generally at or near the methods reporting limit. As such, the method is particularly susceptible to positive interferences from the presence of low levels cyanide residues on glassware from previous analyses of samples and/or various QC samples and standards with elevated PAC concentrations. Thus, frits, absorber tube, and condensers should be cleaned with dilute HCl and then rinsed with distilled water **between** samples.

**5.0 Cyanide Analysis**

The entire contents of the absorber tube are transferred to a 250 mL volumetric flask. The tube is rinsed with distilled water, with the rinsate added to the flask. The absorbing solution is then brought to volume with distilled water.

Cyanide analysis can be performed colorimetrically by the autoanalyzer method following the methodologies and requirements of SW-846 Method 9014 or the CLP SOW 335.2 or the titrimetric method specified in Standard Method 4500-CN D. Solutions having high cyanide concentrations are diluted manually using NaOH solution and volumetric glassware.
*Analytical Note*: Unanalyzed distillates may be stored in tightly sealed flasks at 4 ± 2° C for up to 24 hours.

**6.0 PAC Method Quality Control Criteria**

One method blank sample must be run with each analytical batch of up to 20 samples.

One aqueous KCN standard (50 µg CN; 50 µL of 1000 ppm stock solution) must be run with each analytical batch of up to 20 samples. The Percent Recovery (% R) for this quality control sample, designated as the Positive Laboratory Control Sample (LCS-P), must be 80-120% of the true value (0.1 mg/L).

One solid Prussian Blue standard (500 µg cyanide; 0.0012 g of Prussian Blue) must be run with each analytical batch of up to 20 samples. The % R for this quality control sample, designated as the Negative Laboratory Control Sample (LCS-N), must be ≥ 10% of the true value (1.0 mg/L).

If either of these batch QC samples, LCS-P or LCS-N, fails to meet their criteria, the sample batch must be re-run. It may be necessary to modify the temperature and/or flow conditions so that both of the QC samples, LCS-P or LCS-N, are able to comply with the method's QC criteria.

**7.0 PAC Method Performance Criteria**

Compliance with the LCS-P and LCS-N quality control requirements described in Section 6.0 is the basis for evaluation of satisfactory method performance. Conformity with the above referenced temperature and flow rate guidelines, together with other specific analytical specifications, is expected under most circumstances to produce results that will satisfy PAC method quality control requirements. However, it is expected that some laboratories will be able to satisfy method QC requirements even with modifications of the method's temperature and flow rate guidelines. For instance, one laboratory that assisted the Department in method development was consistently able to meet or exceed method LCS-P and LCS-N quality control requirements, as well as for routine calibration, ICV, and CCV requirements, for sample batches run at 72 ° C with a flow rate of 325-350 mL/min.

## 8.0 Sample Collection, Preservation, And Handling Procedures for PAC Analysis

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil/sediment and waste samples for PAC analyses conducted in support of MCP decision-making are described below in Table 1.

**Table 1 Holding Times and Preservatives for PAC Samples**

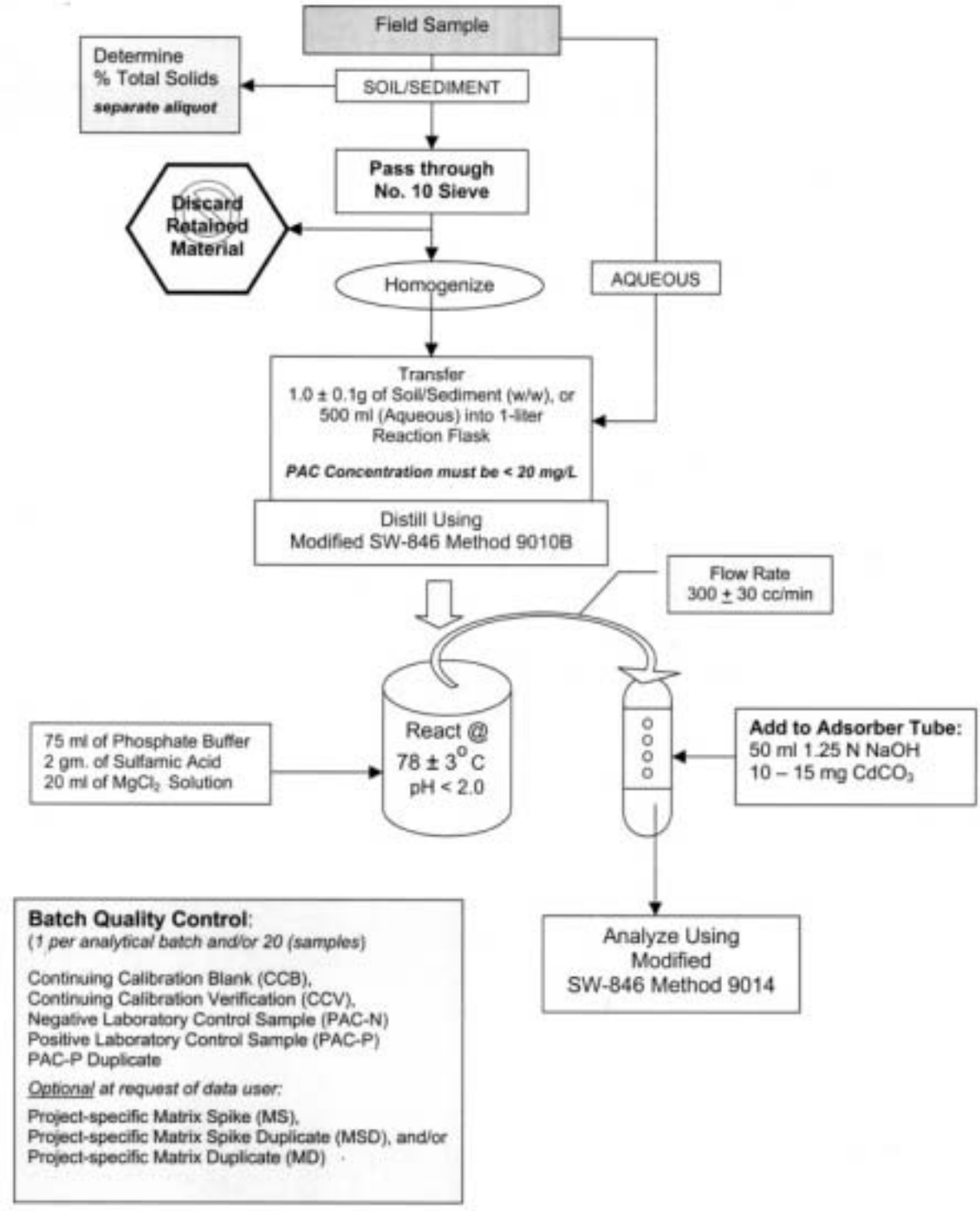
| {PRIVATE} Matrix | Container | Preservation | Holding Time |
|---|---|---|---|
| Aqueous Samples | 250 mL Polyethylene for mini-distillation procedure;<br>1 L Poly for maxi-distillation | NaOH to pH ≥ 12.0.<br>Cool to 4 ± 2°, 0.6 g ascorbic acid per liter, if residual chlorine is suspected | 14 days |
| Soil/Sediments Samples | 4-ounce glass jar with inert (Teflon) liner | Cool to 4 ± 2° C | 14 days |
| Waste Samples [a,b] | 250 mL amber wide-mouth jar with inert (Teflon) liner | Cool to 4 ± 2° C.<br>Keep out of direct light | Soon as Possible |

a. Reactive Cyanide waste defined as 250 mg/kg of Releasable Cyanide as measured by SW-846, Chapter Seven, Section 7.3.3

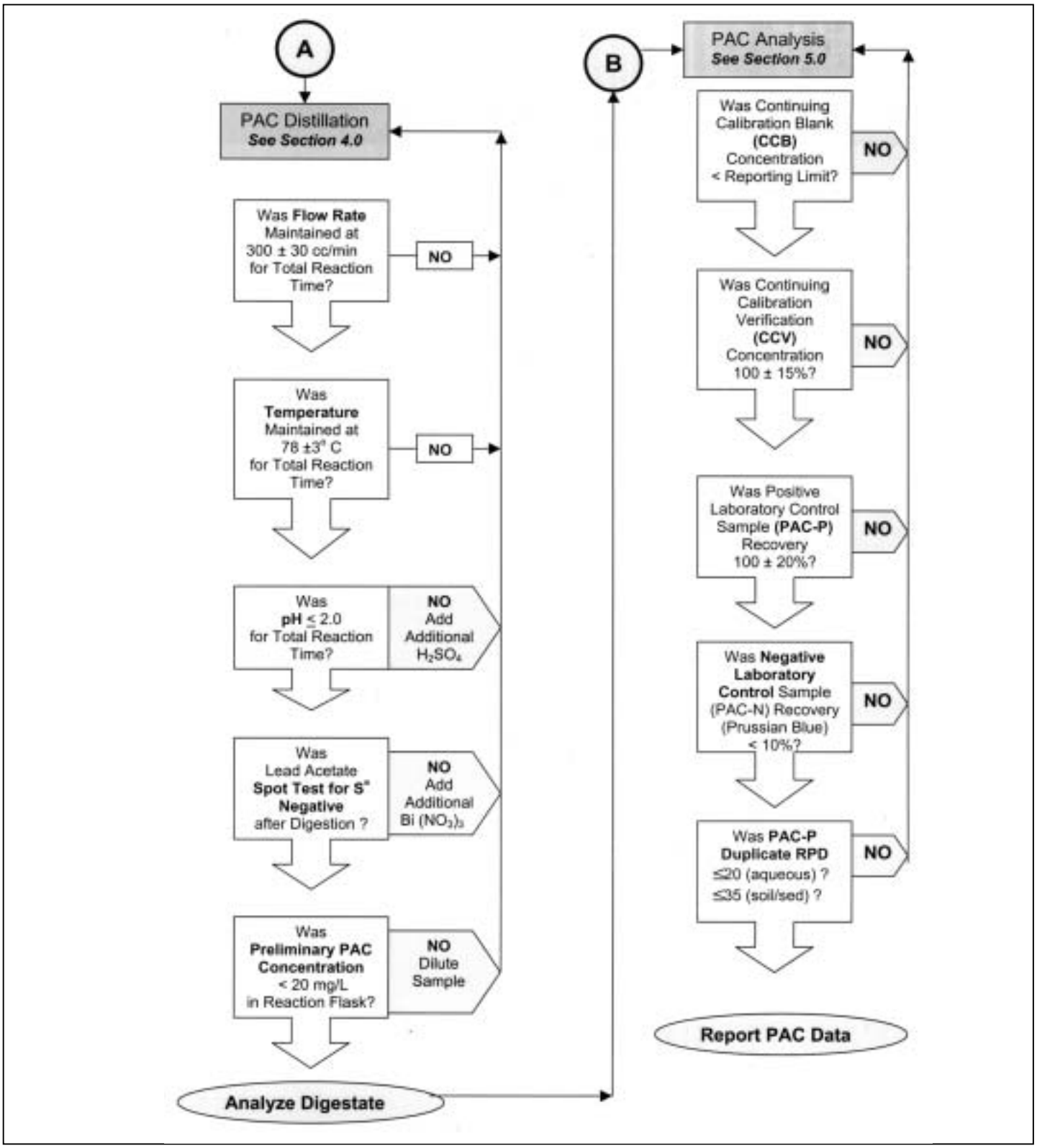
b. Samples containing, or suspected of containing, cyanide or a combination of cyanide and sulfide wastes should be collected with a minimum of aeration. The sample container should be filled completely, excluding all head space, and capped. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

***Transcribed 29 January 2003 with minor edits on 30 July 2004 (DGM)***

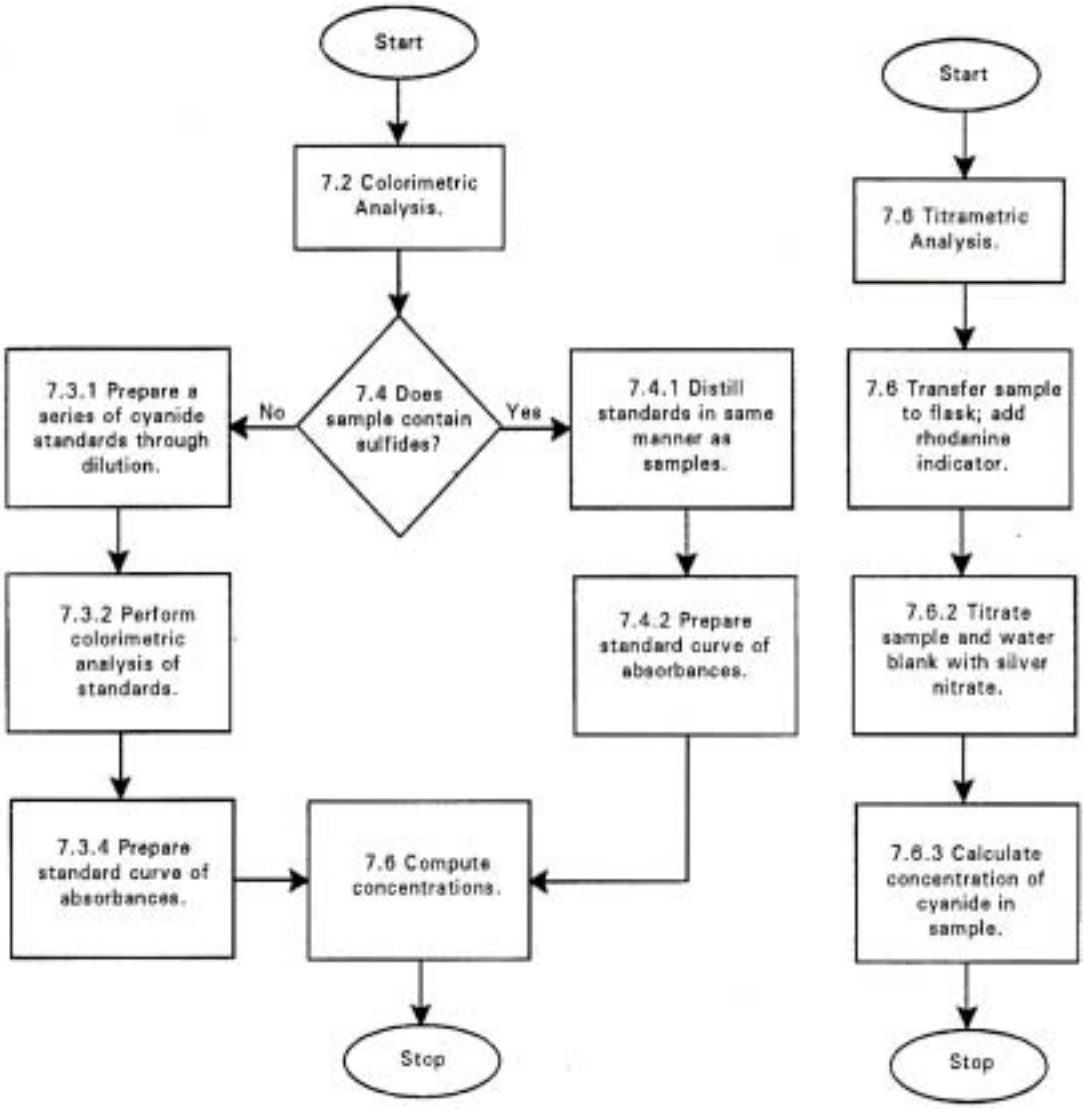
## Physiologically Available Cyanide (PAC) Analytical Flow Chart



## Physiologically Available Cyanide (PAC) QC Flow Chart



**Quality Control Flow Chart Titrimetric and Manual Spectrophotometric Determinative Methods for Cyanide***




* Figure From SW-846 Method 9014
Numbers in individual QC Flow Chart steps refer to corresponding Section Numbers in SW-846 Method 9014